



Superconformal Silver Deposition Using KSeCN Derivatized Substrates

B. C. Baker,^{a,*} C. Witt,^b D. Wheeler,^a D. Josell,^a and T. P. Moffat^{a,*}

^aNational Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

^bInternational Sematech, Austin, Texas

Superconformal filling of submicrometer trenches was achieved using substrates that were catalyzed with KSeCN prior to metal deposition in a catalyst-free, silver-cyanide electrolyte. The degree of superfill was dependent on the time the specimen spent in the KSeCN-containing solution prior to electrodeposition. Longer derivatization times correspond to higher initial catalyst coverages. The feature filling results were consistent with the curvature enhanced accelerator coverage mechanism of superconformal deposition. This mechanism implies that area changes during deposition in a feature lead to higher catalyst coverage at the bottom of the feature, thus enhancing the deposition rate and allowing bottom-up fill.

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Manuscript submitted November 13, 2002; revised manuscript received January 15, 2003. Available electronically February 28, 2003.

Successful implementation of copper interconnect metallization has generated interest in the potential application of silver which has an even higher electrical conductivity and thus the promise of a lower resistance-capacitance (RC) circuit time constant. Recently, it has been shown that seam or void-free filling of vias and trenches with silver is possible in silver cyanide electrolytes containing a selenium-based catalyst.¹⁻³ The evolution of the growth front during feature filling was well explained by the curvature enhanced accelerator coverage (CEAC) mechanism that has also been used to quantify superconformal copper electrodeposition.^{4,5} The essence of the CEAC mechanism is that (i) the local deposition rate is determined by the catalyst coverage and (ii) the partitioning of the catalyst between the free-surface and the bulk deposit, *i.e.*, incorporation, consumption, or desorption, represents a small perturbation relative to coverage changes induced by electrode shape change during metal deposition in submicrometer features. Thus, the diminishing area associated with growth at the bottom of a trench or via results in an increase in catalyst coverage and thus "bottom-up" filling of the features. For superconformal silver deposition, a model $\text{KAg}(\text{CN})_2$ -KCN-KSeCN electrolyte was identified where accumulation of a selenium adsorbate at the interface, most likely SeCN⁻, resulted in catalysis of the metal deposition reaction.

In the conventional one-step superfilling process the catalyst accumulates at the interface by adsorption during the plating process.¹⁻³ This initial period of catalyst accumulation from the electrolyte delays the onset of superconformal filling; in contrast, derivatization of the electrode with the catalyst prior to electroplating allows the curvature-related bottom-up filling dynamic to proceed from the first moment of deposition, thereby allowing the filling of higher aspect ratio features. This strategy has been successfully employed for copper superfilling.⁶ An additional advantage of the two-step process is the minimization, or avoidance of aging issues, which often accompany the use of catalytic additives in plating electrolytes.

This work describes feature filling of specimens derivatized in a catalyst-containing solution and subsequently plated in a catalyst-free silver-cyanide electrolyte. The catalyst coverage was established by derivatization for different times in a KSeCN electrolyte.

Experimental

The silver-cyanide electrolytes used for all experiments contained 0.23 mol/L $\text{KAg}(\text{CN})_2$ and 3.4 mol/L KCN. The electrochemical cell consisted of a silver reference electrode and a platinum counter electrode (area = 18 cm²) immersed in a beaker containing 0.1 L of electrolyte open to the laboratory atmosphere. All cited potentials are overpotentials relative to the silver reference.

Substrates with patterned trench test structures were cleaved from wafers provided by International Sematech. The trenches were lined with a TiN barrier layer and a ~100 nm thick sputtered copper seed layer (thickness given is that on the field above the features). The patterned substrates were plated with a thin conformal silver layer that was used as a seed for subsequent experiments. The silver seed layers were deposited at -0.3 V for 30 s in the silver-cyanide electrolyte, and the specimens were then rinsed with distilled water and dried with N₂. The resulting seed is approximately 40 nm thick on all surfaces (trench bottom and sidewalls, and field) based on the deposition charge and examination of cross-sectioned specimens by scanning electron microscopy (SEM, as shown in Fig. 1). The silver seed permits catalyst adsorption on silver (instead of copper) to be the reference point in all subsequent experiments. Experiments without the silver seed layer also revealed artifacts that possibly indicated contamination of the electrolyte with cupric ion due to corrosion of the copper seed.

The silver seeded substrates were derivatized with the selenium catalyst by open-circuit immersion in a silver-cyanide electrolyte containing a catalyst concentration of 20 μmol/L of KSeCN for 5, 10, 15, or 30 s. They were then rinsed in distilled water and dried with N₂. The specimens were next immersed in a catalyst-free silver-cyanide electrolyte for superfilling experiments that occurred within 10 min of the derivatization treatment. Silver was electrode-

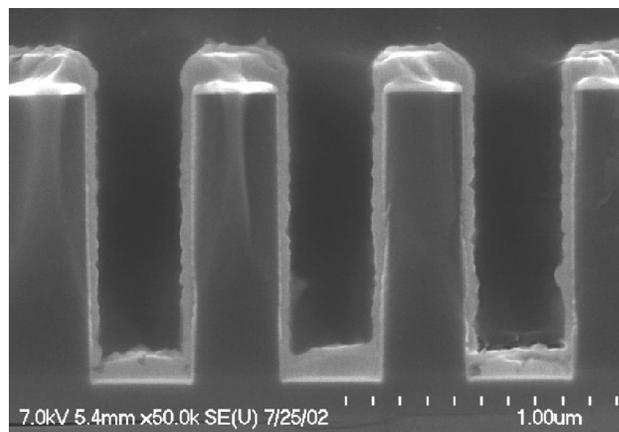


Figure 1. SEM images showing trenches of aspect ratio ≈ 3.5 after the ≈ 40 nm silver seed layer has been deposited in a silver-cyanide electrolyte (0.23 mol/L $\text{KAg}(\text{CN})_2$ and 3.4 mol/L KCN). The copper seed on which the silver seed is electrodeposited is much thinner on the sidewalls than on the field over the trench and the trench bottom (typical of sputter-deposited seed layers). Corrosion of the copper seed that occurred during the silver seed layer deposition is visible.

* Electrochemical Society Active Member.

^z E-mail: brett.baker@nist.gov

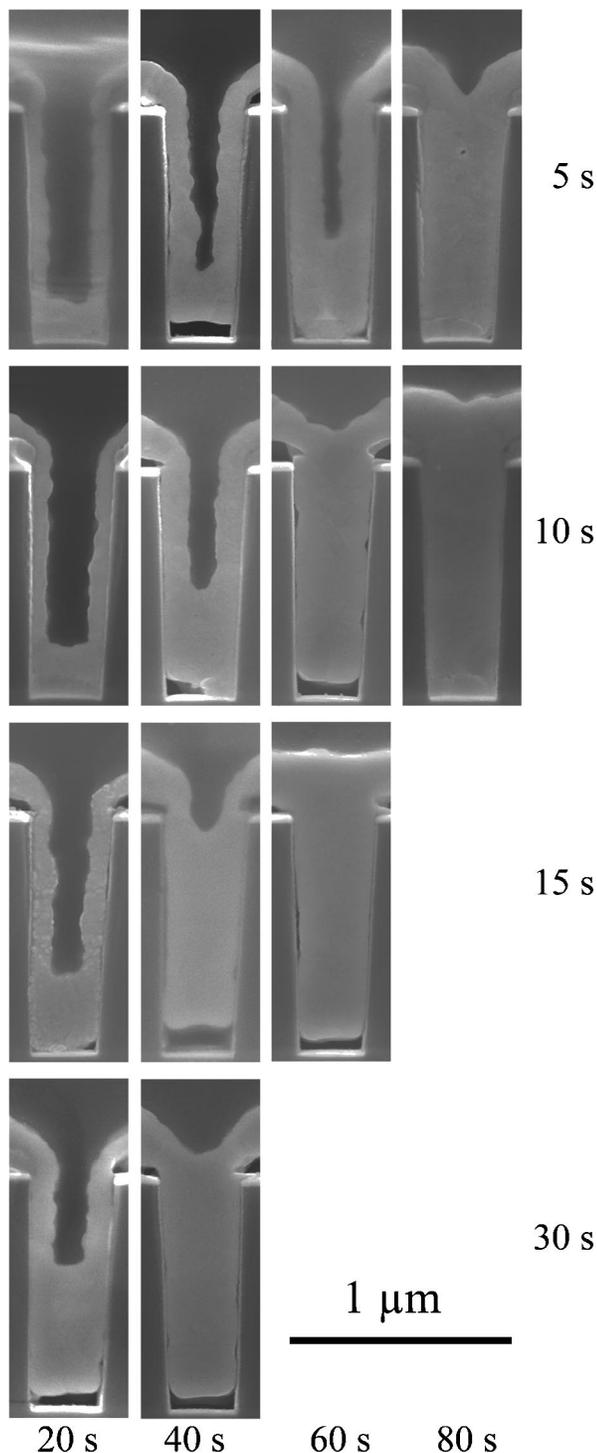


Figure 2. SEM images showing sequential filling of trenches of aspect ratio ≈ 3.5 in a silver-cyanide electrolyte ($0.23 \text{ mol/L KAg(CN)}_2$ and 3.4 mol/L KCN). The specimens, with a silver seed previously deposited, were derivatized in a silver-cyanide solution containing $20 \text{ }\mu\text{mol/L KSeCN}$ for the time indicated (vertical axis). The specimens were dried and then transferred for silver deposition in a catalyst-free electrolyte for the times indicated (horizontal axis). Bottom-up superconformal filling is evident for the three longer derivatization times.

posited at an overpotential of -0.2 V for times ranging between 20 and 80 s.

After plating, the patterned specimens were covered in epoxy and a glass coverslip and cross-sectioned. Polishing was accom-

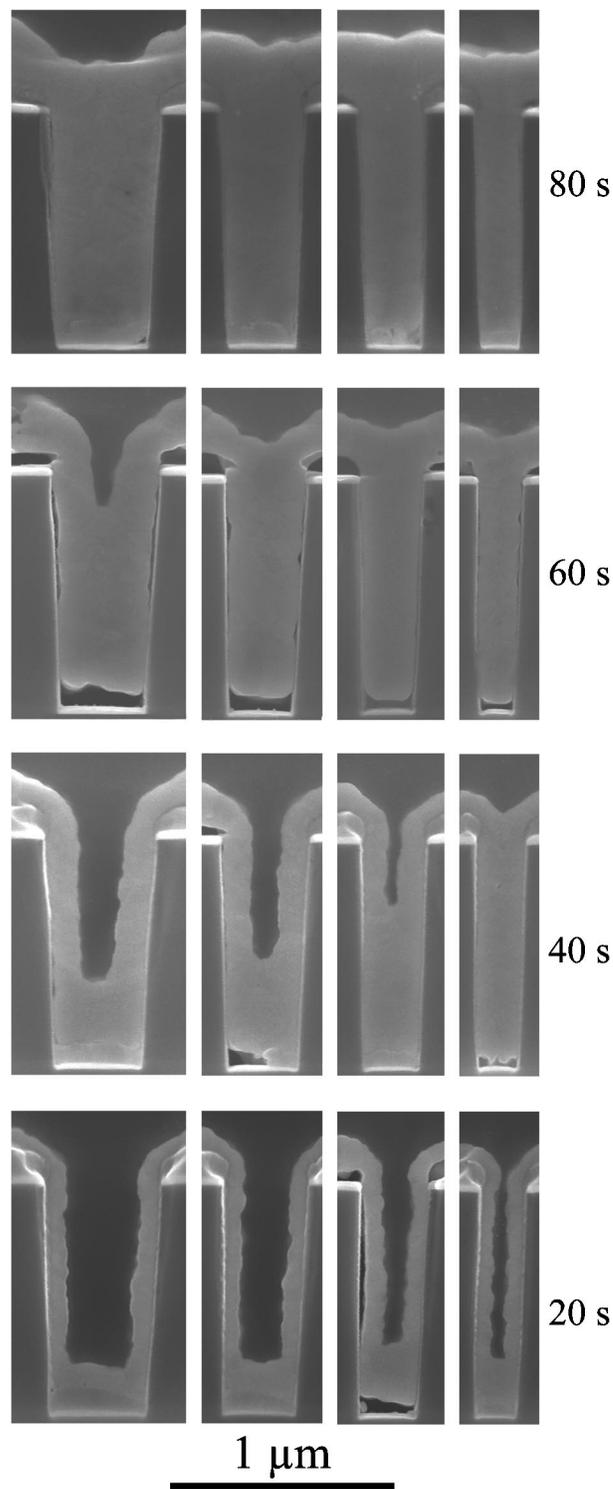


Figure 3. SEM images showing sequential filling of trenches electrodeposited in a silver-cyanide electrolyte ($0.23 \text{ mol/L KAg(CN)}_2$ and 3.4 mol/L KCN). The specimens, with a silver seed already deposited, were derivatized in a silver-cyanide solution containing $20 \text{ }\mu\text{mol/L KSeCN}$ for 10 s prior to silver deposition in a catalyst-free electrolyte for the times indicated (vertical axis). The aspect ratios of the trenches are approximately: 2.4, 2.8, 3.5, and 4.6 (left to right) without the silver seed. Superconformal filling is achieved for all but the narrowest (highest aspect ratio) trench.

plished using diamond lapping films down to $0.05 \text{ }\mu\text{m}$ grit followed by Ar^+ ion polishing at 13° from the plane of the specimen. Specimens were studied using a scanning electron microscope with a field emission source.

Results and Discussion

Figure 2 displays trench filling as a function of derivatization time and deposition time for a height/width aspect ratio of approximately 3.5. Silver deposition on specimens derivatized for 5 s yields conformal filling, midfeature voiding, and a sharp cusp as the growth front advances beyond the trench. In contrast, bottom-to-top superconformal filling of the features is evident when silver is deposited on specimens derivatized for 10, 15, and 30 s. For these cases, the longer the derivatization time (*i.e.*, the higher the initial catalyst coverage), the more rapid the deposition on all surfaces and the earlier the onset of bottom-up fill. The tell-tale cusp visible over the conformally filled feature does not form over the superconformally filled features.

Corrosion of the original copper seed layer and delamination from the barrier layer are visible in several images. These artifacts have already been noted to occur during the silver seed layer deposition and to be limited to the underlying copper seed layer (Fig. 1). Consistently, they do not materially affect filling in any of the features, as demonstrated by the absence of voids extending from the sidewalls or bottom into the silver deposits. These defects may presumably be eliminated by using a simple silver seed layer as opposed to the bilayer copper-silver seed used here.

The influence of aspect ratio on the filling process was also examined as shown in Fig. 3. The aspect ratios of these features were approximately: 2.4, 2.8, 3.5, and 4.6 (left to right). The stated ratios pertain to the widths of the features at their midplane prior to Ag seed deposition. The cross sections reveal that a 10 s derivatization time is sufficient for superfilling trenches up to an aspect ratio of approximately 3.5. Bottom-up filling is seen to occur at earlier times in the smaller features. However, small voids are apparent in the 40 and 60 s cross sections of the narrowest feature indicating that the superfilling dynamic is insufficient for complete filling of this high aspect ratio. As with Fig. 2, the delamination apparent in some of the images in Fig. 3 is an artifact of the silver seed-layer deposition process and is not relevant to superfilling *per se*.

An important observation follows from these simple experiments. Specifically, the shape evolution observed during feature filling of the derivatized electrodes is qualitatively indistinguishable from results obtained in a single electrolyte containing the catalyst.¹⁻³ All characteristics of the filling process observed in Fig. 2 and 3 have been predicted previously by the CEAC mechanism of superfilling for deposition in catalyst-containing electrolytes, as revealed in simulations for this as well as related systems.¹⁻⁶ Particular

examples include the transition from conformal to superconformal filling with increasing catalyst coverage,⁴ the concurrent decrease of the period of conformal deposition,³ which is also consistent with the previously demonstrated relationship between silver deposition rate and adsorbed Se-based catalyst,¹ and the bottom-to-top superconformal deposition itself.

The two-step process of catalyst derivatization followed by metal deposition in a catalyst-free electrolyte allows the partitioning or consumption of the catalyst to be studied systematically. The use of submonolayer derivatization also sets an upper bound on the "contamination" of the deposited silver. Finally, as with previous work on superconformal copper deposition, these experiments demonstrate that the differential reactivity responsible for superfilling is the outcome of geometrically determined changes in surface chemistry (CEAC mechanism) that have little to do with homogeneous chemistry. Detailed study of the kinetics of catalyst adsorption and deactivation will be the subject of future efforts.

Conclusion

Superconformal filling of submicrometer trenches may be achieved by first derivatizing the surface with a selenium catalyst and then electrodepositing silver from a catalyst-free silver-cyanide electrolyte. Filling is seen to be a function of the derivatization time. This process allows higher aspect ratio features to be filled than can be accomplished from a conventional catalyst-containing electrolyte. Finally, catalyst derivatization followed by metal deposition offers an alternative route toward process control.

The National Institute of Standards and Technology assisted in meeting the publication costs of this article.

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